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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁶ : C11D 3/48, 3/18, 3/43, A01N 33/12 // 65/00, 25/02		A1	(11) International Publication Number: WO 99/28428
			(43) International Publication Date: 10 June 1999 (10.06.99)
(21) International Application Number: PCT/US98/22783		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 27 October 1998 (27.10.98)			
(30) Priority Data: 9725091.4 28 November 1997 (28.11.97) GB 9725098.9 28 November 1997 (28.11.97) GB 9725093.0 28 November 1997 (28.11.97) GB			
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(54) Title: CONCENTRATED LIQUID CLEANER FOR HARD SURFACES			
(57) Abstract Concentrated liquid cleaning and/or disinfectant compositions which are normally diluted in a larger volume of water to form a working solution therefrom, and which exhibit a blooming effect when diluted. The compositions are aqueous, and include a terpene based solvent or a pine oil constituent; an organic solvent constituent; a binary co-solvent system comprising alkyl diphenyl solvent and a co-solvent; and optionally, a germicidal cationic surfactant, an amine oxide surfactant, one or more further optional constituents selected from chelating agents, coloring agents, light stabilizers, fragrances, thickening agents, hydrotropes, pH adjusting agents, pH buffers and one or more deterative surfactant constituents.			

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CONCENTRATED LIQUID CLEANER FOR HARD SURFACES

The present invention relates to disinfectant compositions. More particularly the present invention relates to concentrated liquid disinfectant compositions which are normally diluted in a larger volume of water to form a working solution therefrom, and which exhibit a blooming effect when diluted.

Blooming is a property exhibited by dilutable compositions such as known cleaning compositions, specifically pine-oil type cleaning compositions which contain a significant amount (generally at least about 5% and more) of pine oil. Certain phenolic disinfectant compounds, such as LYSOL disinfectant concentrate (Reckitt & Colman, Inc., Montvale NJ) also exhibit such a blooming property. Blooming may be characterized as the formation of milky, creamy or cloudy appearance which is manifested when a dilutable composition is added to a larger volume or quantity of water. Blooming is an important characteristic from a consumer standpoint, as it is perceived to be an indicator of efficacy.

According to a first aspect of the invention there is provided an aqueous concentrated liquid disinfectant composition which blooms when added to a larger volume of water which comprises the following constituents:

pine oil constituent;
germicidal cationic surfactant, preferably a quaternary ammonium compound having germicidal properties;
organic solvent constituent;
binary co-solvent system comprising alkyl diphenyl solvent and a co-solvent;
optionally but desirably at least one optional constituent selected from:
chelating agents, coloring agent, light stabilizers, fragrances, thickening agents, hydrotropes, pH adjusting agents, pH buffers one or more deterative surfactant constituents, particularly non-ionic and amphoteric surfactants. The one or more optional constituents are selected to not undesirably affect the overall blooming characteristics of the present inventive compositions.

According to a second aspect of the invention there is provided aqueous concentrated liquid hard surface cleaning composition which blooms when added to a larger volume of water which comprises the following constituents:

pine oil constituent;
organic solvent constituent;
binary co-solvent system comprising an alkyl diphenyl solvent and a co-solvent;
an amine oxide surfactant constituent;
optionally but desirably at least one optional constituent selected from:
chelating agents, coloring agents, light stabilizers, fragrances, thickening agents, hydrotropes, pH adjusting agents, pH buffers one or more deterative surfactant constituents, particularly non-ionic and amphoteric surfactants. The one or more

optional constituents are selected to not undesirably affect the overall blooming characteristics of the present inventive compositions.

According to a third aspect of the invention there is an aqueous concentrated liquid disinfectant composition which blooms when added to a larger volume of water which comprises the following constituents:

- a terpene based solvent;
- germicidal cationic surfactant, preferably a quaternary ammonium compound having germicidal properties;
- organic solvent constituent;
- a binary co-solvent system comprising alkyl diphenyl solvent and a co-solvent; one or more nonionic surfactants;
- optionally but desirably at least one optional constituent selected from: chelating agents, coloring agents, light stabilizers, fragrances, thickening agents, hydrotropes, pH adjusting agents, pH buffers one or more deterative surfactant constituents, particularly non-ionic and amphoteric surfactants, as well as others known the art and useful in similar compositions; and,
- the balance being water.

In preferred embodiments of the third aspect of the invention, the terpene based solvent constituent is present with respect to the alkyl diphenyl solvent in a respective weight ratio of from 8:1 to 1:2, with the total amount of these combined constituents not exceeding 9%wt. of the total weight of the concentrate compositions. This third inventive aspect demonstrates compositions with good blooming characteristics, but with relatively reduced amounts of pine oil or terpene based solvent.

Processes for the cleaning and/or disinfecting of hard surfaces using any of the inventive compositions taught herein are also contemplated to form part of the invention.

In preferred embodiments the concentrate compositions provide excellent initial blooming characteristics in 'as mixed' dilutions with water, but also exhibit good retention of blooming characteristics over a longer time period, viz., days and weeks.

It is a still further object of the invention to provide such a concentrated liquid disinfectant composition, such as according to the first aspect of the invention, which in a diluted form provides disinfection of surfaces wherein the presence of gram positive type pathogenic bacteria such as *Staphylococcus aureus*, and/or the presence of gram negative type pathogenic bacteria such as *Escherichia coli* and/or *Pseudomonas aeruginosa* is suspected.

Terpene based solvent

The terpene based solvent constituent, includes one or more further terpene based solvents. These terpene based solvents preferably contain mono- and bicyclic monoterpenes, i.e., those of the hydrocarbon class, which include, for example, the terpinenes, terpinolenes, limonenes, pinenes and mixtures thereof. Useful terpenes

include d-limonene, and the mixture of terpene hydrocarbons obtained from the essence of oranges, e.g., cold-pressed orange terpenes and orange terpene oil phase ex fruit juice, and the mixture of terpene hydrocarbons expressed from lemons and grapefruit. Numerous other terpene hydrocarbons are known to those skilled in the art and may be used to prepare the blooming type, germicidal hard surface cleaning and disinfecting compositions of the present invention; however, those as mentioned above recited which are based on d-limonene and the mixture of terpene hydrocarbons obtained from citrus fruits are the most readily available and, hence, are preferred. Of these d-limonene is the most preferred.

These terpene containing solvent constituents particularly useful according to the third aspect of the invention are typically supplied as technical grade materials which may be and are often formulated with small amounts, e.g., 0.1%wt. (weight percent,) of auxiliary materials such as one or more stabilizers, e.g., antioxidants such as butylated hydroxytoluene. Such auxiliary materials are included within the meaning of the term "terpene containing solvent", as employed in this specification and the accompanying claims.

The concentrate compositions of the third aspect of the invention desirably comprise a terpene based constituent which may be a pine oil constituent, or a d-limonene constituent or which may include both these materials. Pine oil is an organic solvent, and is a complex blend of oils, alcohols, acids, esters, aldehydes and other organic compounds, and may be used as part of, or all of the terpene based solvent constituent. Preferred pine oil preparations which comprise at least about 50% terpene alcohols, more desirably at least about 60% terpene alcohols.

Particularly useful d-limonene containing compositions include those described above.

The terpene containing solvent constituent may be present in the concentrate compositions according to the third aspect of the invention in amounts of from about 0.001 % by weight to up to about 20% by weight, preferably about 0.1 - 15% by weight, most preferably in amount of between 1 - 12% by weight.

According to certain preferred embodiments of the third aspect of the invention, the terpene solvent constituent is solely a d-limonene constituent.

According to certain preferred embodiments of the third aspect of the invention, the terpene solvent constituent is solely a pine oil constituent, especially the preferred pine oil preparations described above.

Pine oil constituent

The concentrate compositions of the first and second aspects of the invention comprise a pine oil constituent. This pine oil constituent may also be present in compositions according to the third aspect of the invention. Pine oil is an organic solvent, and is a complex blend of oils, alcohols, acids, esters, aldehydes and other organic compounds. These include terpenes which include a large number of related alcohols or ketones. Some important constituents include terpineol, which is one of

three isomeric alcohols having the basic molecular formula $C_{10}H_{17}OH$. Useful pine oils include synthetic pine oil, and also include steam distilled and sulfate pine oils, and will generally contain a higher content of turpentine alcohols. Other important compounds include alpha- and beta-pinene (turpentine), abietic acid (rosin), and other isoprene derivatives.

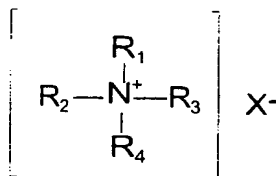
Particularly effective pine oils which are presently commercially available include those in the GLIDCO Pine Oil series, which includes grades "60", "80", "150", "SW", "350" having respectively 60%wt., 80%wt., 85%wt., 75%wt. and 100%wt. of terpene alcohols, (which is sometimes referred to as alpha-terpineol) especially

The pine oil constituent may be present in the concentrate compositions of the first and second aspects of the invention in amounts of from about 0.001 % by weight to up to about 20% by weight, preferably about 0.1-15% by weight, most preferably in amount of between 1-12 % pine oil by weight. Preferred of these are pine oil preparations which comprise at least about 50% terpene alcohols (alpha-terpineols), more desirably at least about 60% terpene alcohols, and more preferably those which comprise at least about 80% terpene alcohols.

Germicidal cationic surfactant

The concentrate compositions according to the first and third aspects of the invention include as a necessary constituent at least one cationic surfactant which is found to provide a broad antibacterial or sanitizing function. Any cationic surfactant which satisfies these requirements may be used and are considered to be within the scope of the present invention.

Examples of preferred cationic surfactant compositions useful in the practice of the instant invention are those which provide a germicidal effect to the concentrate compositions, and especially preferred are quaternary ammonium compounds and salts thereof, which may be characterized by the general structural formula:

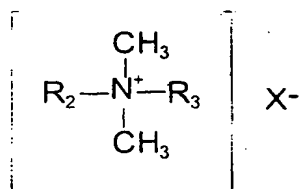


wherein at least one of R_1 , R_2 , R_3 and R_4 is a alkyl, aryl or alkylaryl substituent of from 6 to 26 carbon atoms, and the entire cation portion of the molecule has a molecular weight of at least 165. The alkyl substituents may be long-chain alkyl, long-chain alkoxyaryl, long-chain alkylaryl, halogen-substituted long-chain alkylaryl, long-chain alkylphenoxyalkyl, arylalkyl, etc. The remaining substituents on the nitrogen atoms other than the abovementioned alkyl substituents are hydrocarbons usually containing no more than 12 carbon atoms. The substituents R_1 , R_2 , R_3 and R_4 may be straight-chained or may be branched, but are preferably straight-chained, and may include one

or more amide, ether or ester linkages. The counterion X may be any salt-forming anion which permits water solubility of the quaternary ammonium complex.

Exemplary quaternary ammonium salts within the above description include the alkyl ammonium halides such as cetyl trimethyl ammonium bromide, alkyl aryl ammonium halides such as octadecyl dimethyl benzyl ammonium bromide, N-alkyl pyridinium halides such as N-cetyl pyridinium bromide, and the like. Other suitable types of quaternary ammonium salts include those in which the molecule contains either amide, ether or ester linkages such as octyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride, N-(laurylcocoaminoformylmethyl)-pyridinium chloride, and the like. Other very effective types of quaternary ammonium compounds which are useful as germicides include those in which the hydrophobic radical is characterized by a substituted aromatic nucleus as in the case of lauryloxyphenyltrimethyl ammonium chloride, cetylaminophenyltrimethyl ammonium methosulfate, dodecylphenyltrimethyl ammonium methosulfate, dodecylbenzyltrimethyl ammonium chloride, chlorinated dodecylbenzyltrimethyl ammonium chloride, and the like.

Preferred quaternary ammonium compounds which act as germicides and which are be found useful in the practice of the present invention include those which have the structural formula:



wherein R₂ and R₃ are the same or different C₈-C₁₂alkyl, or R₂ is C₁₂₋₁₆alkyl, C₈₋₁₈alkylethoxy, C₈₋₁₈alkylphenoethoxy when R₃ is benzyl, and X is a halide, for example chloride, bromide or iodide, or is a methosulfate anion. The alkyl groups recited in R₂ and R₃ may be straight-chained or branched, but are preferably substantially linear.

Particularly useful quaternary germicides include compositions which include a single quaternary compound, as well as mixtures of two or more different quaternary compounds, such as blends of alkyl dimethyl benzyl ammonium chlorides. Exemplary useful quaternary ammonium compounds include those available under the tradenames BARDAC, BARQUAT, HYAMINE, LONZABAC (ex. Lonza Inc., or Stepan Co.)

The germicidal cationic surfactant, especially the preferred quaternary ammonium salts described above may be present in any germicidally effective concentration. Advantageously, the germicidal cationic surfactant, when present, may be present in the concentrate compositions in amounts of from about 0.001 % by weight to up to about 15% by weight, preferably about 0.01-10% by weight, most preferably in amount of between about 0.5 - 8 % by weight.

Organic Solvent constituent

A further constituent according to the invention is an organic solvent. This organic solvent, which is present in addition to the pine oil (which is itself known to be an organic solvent) assists in improves the dispersability and/or miscibility of the water insoluble pine oil in water. The organic solvent may also improve the miscibility of further constituents according to the present invention, including any water insoluble or poorly soluble constituents. Many useful organic solvents which are known to be useful in dispersing pine oil in water may be used; virtually any may be used as long as it does not undesirably disrupt the favorable characteristics of the invention, especially the blooming characteristic. Mixtures of two or more organic solvents may also be used as the organic solvent constituent.

Useful organic solvents are those which are at least partially water-miscible such as alcohols, water-miscible ethers (e.g. diethylene glycol diethylether, diethylene glycol dimethylether, propylene glycol dimethylether), water-miscible glycol ether (e.g. propylene glycol monomethylether, propylene glycol mono ethylether, propylene glycol monopropylether, propylene glycol monobutylether, ethylene glycol monobutylether, dipropylene glycol monomethylether, diethyleneglycol monobutylether), lower esters of monoalkylethers of ethyleneglycol or propylene glycol (e.g. propylene glycol monomethyl ether acetate) These materials are all commercially available (ex. Union Carbide, Dow, or Hoechst) Mixtures of organic solvents can also be used.

Particularly useful organic solvents include glycols such as alkylene glycols such as propylene glycol, and glycol ethers. Examples of such glycol ethers include those having the general structure $R'-O-R''-OH$, wherein R' is an alkyl of 1 to 20 carbon atoms, or is aryl, or is alkaryl of at least 6 carbon atoms, and R'' is an ether condensate of propylene glycol and/or ethylene glycol having from one to ten glycol monomer units. Examples of such useful glycol ethers include propylene glycol methyl ether, dipropylene glycol methyl ether, tripropylene glycol methyl ether, propylene glycol isobutyl ether, ethylene glycol methyl ether, ethylene glycol ethyl ether, ethylene glycol butyl ether, diethylene glycol phenyl ether, propylene glycol phenol ether, and mixtures thereof. Preferred are ethylene glycol n-butyl ether, diethylene glycol n-butyl ether, and mixtures thereof. Such glycol ethers are presently commercially available from a number of sources including in the DOWANOL™ glycol ethers (ex. Dow Chemical Co.).

Further particularly useful organic solvents monohydric (straight chained or branched) primary, secondary or tertiary lower aliphatic alcohols, especially C_1-C_6 aliphatic primary and secondary alcohols, of which isopropanol is particularly preferred.

It has generally been found the addition of only a minimum effective amount which is found to be effective in dispersing or solubilizing the pine oil constituent and any other aqueous insoluble or poorly soluble constituents in the concentrate compositions is desirably used. Such is due to desire to reduce the amount of volatile

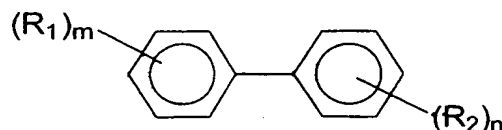
organic constituents in the concentrate compositions of the invention, which volatile organic constituents are desirably minimized from an environmental standpoint. The present inventors have found that inclusion of the organic solvent constituent in amounts of about 0.001% by weight to about 50% by weight have been found to be effective to solubilize the pine oil, as well as in solubilizing other less water soluble constituents present in the concentrate compositions of the invention. Preferably, the organic solvent constituent is present in the concentrate compositions of the invention in amounts of from 0.1 - 40% by weight, and most preferably from about 0.1 - 35% by weight.

Additionally the inventor has found the according to certain preferred embodiments the organic solvent constituent, comprises, and in certain especially preferred embodiments consist essentially of, both an alkylene glycol such as propylene glycol, and a monohydric lower aliphatic alcohol such as a C₁-C₆ aliphatic primary and secondary alcohol, especially isopropyl alcohol.

Binary co-solvent system

The inventive compositions further also include a binary co-solvent system comprising alkyl diphenyl solvent and a co-solvent which aids in the solubilization of the diphenyl solvent in an aqueous medium.

The alkyl diphenyl solvent is one which may be generally represented by the formula



wherein:

R₁ is hydrogen or is a lower alkyl radical, preferably a C₁-C₁₀, but more preferably is a C₁-C₆ straight chained or branched alkyl radical,

R₂ is a lower alkyl radical, preferably a C₁-C₁₀, but more preferably is a C₁-C₆ straight chained or branched alkyl radical,

m is an integer from 1 - 3 inclusive; and,

n is an integer from 1 - 3 inclusive.

Preferably R₁ is hydrogen, m is 1, and R₂ has any of the values indicated above. More preferably, R₁ is hydrogen, m is 1, and R₂ is a C₁-C₆ straight chained or branched alkyl radical. It is to be understood that mixtures of the compounds indicated above may be used as the biphenyl solvent constituent.

Such alkyl diphenyls are, per se, known to the art, and are described in US 3787181. Particularly useful as the alkyl diphenyl solvent are materials presently marketed as NUSOLV ABP solvents (Ridge Technologies Inc., Ridgewood NJ) described to be a high purity alkyl diphenyls and mixtures thereof, and is also available from Koch Chemical Co. (Corpus Christi, TX).

The alkyl diphenyl solvent may be present in the concentrate compositions in amounts of from about 0.001 % by weight to up to about 7% by weight, preferably about 0.01-5 % by weight, most preferably in amount of between 0.1-2 % by weight.

The inventors have observed that the concentrated compositions of the invention are greatly improved with the addition of a co-solvent. This co-solvent aids in the solubilization of the alkyl diphenyl solvent in water is desirably an at least partially water-miscible monohydric linear primary alcohol, especially a water-miscible monohydric primary C₈-C₁₈ alcohol, or is benzyl alcohol. Particularly effective are cetyl, lauryl and myristyl alcohols, and benzyl alcohol. The inventors have found that the inclusion of such alcohols greatly aids in the dissolution of the alkyl diphenyl solvents in the concentrate compositions according to the invention being described herein, which aids in ensuring that clarity of the concentrate composition is maintained which is particularly desirable from a consumer standpoint.

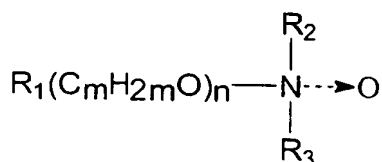
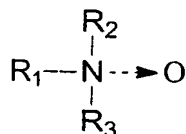
The co-solvent may be present in the concentrate compositions in amounts of from about 0.001 % by weight to up to about 5% by weight, preferably about 0.01-3% by weight, most preferably in amount of between 0.1 - 2% by weight.

Desirably, the binary co-solvent system comprising the alkyl diphenyl solvent and a co-solvent are present in amounts of from 0.001 - 12%wt., more preferably from 0.1 - 12%wt.

Alternately, it is contemplated that the preferred co-solvent described above may be substituted in whole or in part by one or more nonionic or amphoteric surfactants which are also shown to aid in the dissolution of the alkyl diphenyl solvent in water. Such one or more nonionic or amphoteric surfactants include those described below.

25 Amine oxide surfactant

Compositions according to the second aspect of the invention include one or more amine oxide surfactants. Such amine oxides desirably improve the miscibility of the pine oil constituents in the aqueous phase of the concentrate compositions. Non-limiting examples of useful amine oxide semi-polar nonionic surfactants include those according to either of the formulae:



wherein R_1 is hydrogen or is an alkyl, 2-hydroxyalkyl, 3-hydroxyalkyl, or 3-alkoxy-2-hydroxypropyl radical where the alkyl and alkoxy parts contain from about 8 to about 18 carbon atoms, R_2 and R_3 are independently selected from methyl, ethyl, propyl, isopropyl, 2-hydroxyethyl, 2-hydroxypropyl, or 3-hydroxypropyl, m is an integer from 2 to 4, and n is an integer from 0 to about 10. Preferably, the amine oxide semi-polar nonionic surfactants are those according to the formula immediately preceding wherein R_1 is an alkyl radical of from 12 to 16 carbon atoms, R_2 and R_3 are independently selected from methyl or ethyl, m is 2, and n is 0. Specific examples of such useful amine oxide semi-polar nonionic surfactants include cetyl-, myristyl- or lauryl- dimethyl amine oxide or mixtures thereof.

A further useful general class of useful amine oxides which may be included in the amine oxide constituent according to the invention are further alkyl di (lower alkyl) amine oxides in which the alkyl group has about 10-20, and preferably 12-16 carbon atoms, and can be straight or branched chain, saturated or unsaturated. The lower alkyl groups include between 1 and 7 carbon atoms. Examples include those described above, as well as those in which the alkyl group is a mixture of different amine oxides, dimethyl cocoamine oxides, dimethyl (hydrogenated tallow) amine oxides, and myristyl/palmityl dimethyl amine oxides.

A further class of useful amine oxides include alkyl di (hydroxy lower alkyl) amine oxides in which the alkyl group has about 10-20, and preferably 12-16 carbon atoms, and can be straight or branched chain, saturated or unsaturated. Examples are bis(2-hydroxyethyl) cocoamine oxide, bis(2-hydroxyethyl) tallowamine oxide; and bis(2-hydroxyethyl) stearylamine oxide.

Further useful amine oxides include those which may be characterized as alkylamidopropyl di(lower alkyl) amine oxides in which the alkyl group has about 10-20, and preferably 12-16 carbon atoms, and can be straight or branched chain, saturated or unsaturated. Examples are cocoamidopropyl dimethyl amine oxide and tallowamidopropyl dimethyl amine oxide; and

Additional useful amine oxides include those which may be referred to as alkylmorpholine oxides in which the alkyl group has about 10-20, and preferably 12-16 carbon atoms, and can be straight or branched chain, saturated or unsaturated.

Exemplary amine oxide surfactant constituents include AO-728 which is described to be a composition containing 50%wt. of *bis*-(2-hydroxyethyl C₁₂-C₁₅ alkyloxypropyl) amine oxide (ex. Tomah Products Inc., Milton WI), and AMMONYX CDO Special described to be cocoamidopropyl dimethyl amine (ex. Stepan Co., Northfield IL).

The amine oxide constituent is present in the second aspect of the inventive concentrate compositions in amounts of up to 30 %wt., preferably in amounts of from 0.1 - 30%wt. and still more preferably in amounts of from 1 - 20%wt., based on the total weight of the concentrate composition. Particularly preferred amounts are demonstrated in the Examples.

It is to be understood that both the at least partially water-miscible monohydric primary alcohol and an amine oxide may each be present in the concentrate compositions, and according to certain preferred embodiments of the invention both are present.

It is to be understood that the amine oxide, required according to the second aspect of the invention may be included in the first aspect of the invention as an optional constituent.

Nonionic surfactants

According to the third aspect of the invention, there are present one or more nonionic surfactants. These nonionic surfactants may however, be included as one or more of the optional deterative surfactants according to the first and second aspects of the invention.

Practically any hydrophobic compound having a carboxy, hydroxy, amido, or amino group with a free hydrogen attached to the nitrogen can be condensed with ethylene oxide or with the polyhydration product thereof, polyethylene glycol, to form a water soluble nonionic surfactant compound. Further, the length of the polyethylenoxy hydrophobic and hydrophilic elements may various. Exemplary nonionic compounds include the polyoxyethylene ethers of alkyl aromatic hydroxy compounds, e.g., alkylated polyoxyethylene phenols, polyoxyethylene ethers of long chain aliphatic alcohols, the polyoxyethylene ethers of hydrophobic propylene oxide polymers, and the higher alkyl amine oxides.

To be mentioned as particularly useful nonionic surfactants are alkoxyated linear primary and secondary alcohols such as those commercially available under the tradenames PolyTergent® SL series (Olin Chemical Co., Stamford CT), Neodol® series (Shell Chemical Co., Houston TX), Genapol series (Clariant Corp., Charlotte, NC); as well as alkoxyated alkyl phenols including those commercially available under the tradename Triton® X series (Union Carbide Chem. Co., Danbury CT).

Further exemplary useful nonionic surfactants which may be used include alkanolamides including monoethanolamides and diethanolamides, particularly fatty monoalkanolamides and fatty dialkanolamides. Further exemplary nonionic surfactants which may be used include certain alkanolamides including monoethanolamides and diethanolamides, particularly fatty monoalkanolamides and fatty dialkanolamides.

A class of particularly useful nonionic surfactants are those based on alkoxyated, especially ethoxyated, glyceryl esters. Such compounds are known and commercially available. Examples of such materials include alkoxyated glyceryl cocoates, alkoxyated glyceryl tallowates, may of which are available under the tradename VARONIC (Witco Chem. Co., Greenwich CT.) Particularly useful is VARONIC LI-63 which is described to be an alkoxyated glyceryl cocoate which exhibits a hydrophilic/lipophilic balance ('HLB') value of about 15.9.

A further class of particularly useful nonionic surfactants are those based on linear primary alcohol ethoxylates, especially one or those presently commercially

available in the GENAPOL series of surfactants (ex. Clariant Corp., Muttenez, Switzerland)

Nonionic surfactant compositions based on amine oxides described previously are useful in compositions according to the third aspect of the inventive compositions.

5 Most desirably the nonionic surfactant is a mixture of linear primary alcohol ethoxylates and surfactants based on based on alkoxylated, especially ethoxylated, glyceryl esters wherein the amount of the former surfactant exceeds the latter surfactant, and more desirably wherein at least twice of much of the former surfactant is present relative to the latter. Particularly preferred nonionic surfactants, and particularly preferred relative
10 weight ratios are demonstrated by one or more of the Examples.

The nonionic surfactant is desirably present in amounts of from about 0.001 – 12%wt., more preferably in amounts of from about 1-10%wt., and most preferably in amounts of from about 5 –10%wt. in compositions according to the third aspect of the invention.

15 It is to be understood that these nonionic surfactants may be included as optional constituents according to the first and second aspects of the invention.

Water

Water is added in order to provide 100% by weight of the concentrate composition. Water is added in amounts which are sufficient to form the concentrated
20 compositions which amount is sufficient to ensure the retention of a substantially clear characteristic when produced as a concentrate, but at the same time ensuring good blooming upon the addition of the concentrated composition to a further amount of water, or upon the addition of further water to the concentrate. The water may be tap water, but is preferably distilled and/or deionized water.

25 Optional Constituents

The inventive compositions may include one or more further optional constituents. By way of non-limiting examples, these include chelating agents, coloring agents, light stabilizers, fragrances, thickening agents, hydrotropes, pH
30 adjusting agents, pH buffers one or more deterative surfactant constituents particularly non-ionic and amphoteric surfactants. Generally the total weight of such further conventional additives may comprise up to 20% by weight of a concentrated composition formulation.

Further optional, but advantageously included constituents are one or more coloring agents which find use in modifying the appearance of the concentrate
35 compositions and enhance their appearance from the perspective of a consumer or other end user. Known coloring agents, such as a color ranging from colorless to a deep amber, deep amber yellow or deep amber reddish color. Such a coloring agent or coloring agents may be added in any useful amount in a conventional fashion, i.e., admixing to a concentrate composition or blending with other constituents used to form
40 a concentrate composition. However, other colors atypical of pine oil type cleaning concentrates may be used as well. Known art light stabilizer constituents, such as

stilbene derivatives may also be added, particularly wherein coloring agents are used in a composition. As is known to the art, such light stabilizers act to retain the appearance characteristics of the concentrate compositions over longer intervals of time.

5 Exemplary useful buffers include the alkali metal phosphates, polyphosphates, pyrophosphates, triphosphates, tetraphosphates, silicates, metasilicates, polysilicates, carbonates, hydroxides, and mixtures of the same. Certain salts, such as the alkaline earth phosphates, carbonates, hydroxides, can also function as buffers. It may also be suitable to use buffers such materials as aluminosilicates (zeolites), borates,
10 aluminates and certain organic materials such as gluconates, succinates, maleates, and their alkali metal salts. Such buffers keep the pH ranges of the compositions of the present invention within acceptable limits.

Exemplary useful pH adjusting agents include known materials which may be used to adjust the pH of the concentrate compositions to a desired range.

15 The useful optional nonionic surfactants, include known art nonionic surfactant compounds, including those described previously. Practically any hydrophobic compound having a carboxy, hydroxy, amido, or amino group with a free hydrogen attached to the nitrogen can be condensed with ethylene oxide or with the polyhydration product thereof, such as polyethylene glycol, to form a water soluble
20 nonionic surfactant compound. Further, the length of the polyethylenoxy hydrophobic and hydrophilic elements may various. Exemplary nonionic compounds include the polyoxyethylene ethers of alkyl aromatic hydroxy compounds, e.g., alkylated polyoxyethylene phenols, polyoxyethylene ethers of long chain aliphatic alcohols, the polyoxyethylene ethers of hydrophobic propylene oxide polymers, and the higher alkyl
25 amine oxides.

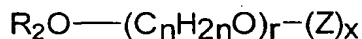
Further exemplary useful nonionic surfactants which may be used include certain alkanolamides including monoethanolamides and diethanolamides, particularly fatty monoalkanolamides and fatty dialkanolamides. Commercially available monoethanol amides and diethanol amides include those marketed under the trade
30 names ALKAMIDE and CYCLOMIDE by Rhône-Poulenc Co., (Cranbury, NJ).

Exemplary nonionic surfactants include certain ethoxylates presently commercially available under the trade name GENAPOL (ex. Clariant Co., Muttentz, Switzerland) which are linear alcohol ethoxylates, as well as NEODOL (Shell Chemical Co., Houston, TX(USA)), which are ethoxylated higher aliphatic, primary ethoxylates.
35 Further useful nonionic surfactant compositions include the condensation products of a secondary aliphatic alcohols containing 8 to 18 carbon atoms in a straight or branched chain configuration condensed with 5 to 30 moles of ethylene oxide. Such are commercially available as TERGITOL surfactants.(Union Carbide Co., Danbury, CT(USA)).

40 Other suitable nonionic surfactant compositions include the polyethylene oxide condensates of one mole of alkyl phenol containing from about 8 to 18 carbon atoms

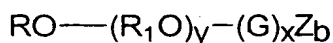
in a straight- or branched chain alkyl group with about 5 to 30 moles of ethylene oxide, including those which are presently commercially available under the trade name of IGEPAL (Rhône-Poulenc, Princeton NJ(USA)). Further useful nonionic surfactants include the water-soluble condensation products of a C₈-C₂₀ alkanol with a mixture of ethylene oxide and propylene oxide wherein the weight ratio of ethylene oxide to propylene oxide is from 2.5:1 to 4:1, preferably 2.89:1 to 3.3:1, with the total of the ethylene oxide; and propylene oxide (including the terminal ethanol or propanol group) being from 60-85%, preferably 70 to 80%, by weight. Such include those commercially available under the trade name of PLURAFAC (BASF Corp., Hackettstown, NJ (USA)). Still further useful water-soluble nonionic surfactants include condensation products of a C₈-C₂₀ alkanols with a mixture of ethylene oxide and/or propylene oxide. Such are commercially available under the tradename POLYTERGENT (Olin Chemical Co., Stamford CT(USA)).

Further suitable water-soluble nonionic surfactants which may also be used include those which are marketed under the trade name PLURONICS (BASF Corp., Mt. Olive Township, NJ (USA)). These are formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. Further useful nonionic surfactants include alkylmonoglycosides and alkylpolyglycosides which are alkaline and electrolyte stable. Such are prepared generally by reacting a monosaccharide, or a compound hydrolyzable to a monosaccharide with an alcohol such as a fatty alcohol in an acid medium. Various glycoside and polyglycoside compounds including alkoxylated glycosides may be used. An exemplary useful polyglycoside is one according to the formula:



where Z is derived from glucose, R is a hydrophobic group selected from alkyl groups, alkylphenyl groups, hydroxyalkylphenyl groups as well as mixtures thereof, wherein the alkyl groups may be straight chained or branched, which contain from about 8 to about 18 carbon atoms, n is 2 or 3, r is an integer from 0 to 10, but is preferably 0, and x is a value from about 1 to 8, preferably from about 1.5 to 5. Preferably the alkylpolyglycosides are nonionic fatty alkylpolyglucosides which contain a straight chain or branched chain C₈-C₁₅ alkyl group, and have an average of from about 1 to about 5 glucose units per fatty alkylpolyglucoside molecule. More preferably, the nonionic fatty alkylpolyglucosides which contain straight chain or branched C₈-C₁₅ alkyl group, and have an average of from about 1 to about 2 glucose units per fatty alkylpolyglucoside molecule.

A further exemplary group of alkyl glycoside surfactants suitable for use in the practice of this invention may be represented by formula I below:



wherein: R is a monovalent organic radical containing from about 6 to about 30, preferably from about 8 to about 18 carbon atoms; R₁ is a divalent hydrocarbon radical containing from about 2 to about 4 carbon atoms; O is an oxygen atom;

- 5 y is a number which has an average value from about 0 to about 1 and is preferably 0; G is a moiety derived from a reducing saccharide containing 5 or 6 carbon atoms; and x is a number having an average value from about 1 to 5 (preferably from 1.1 to 2);

Z is O₂M¹,



O(CH₂), CO₂M¹, OSO₃M¹, or O(CH₂)SO₃M¹; R₂ is (CH₂)CO₂M¹ or CH=CHCO₂M¹; (with the proviso that Z can be O₂M¹ only if Z is in place of a primary hydroxyl group in which the primary hydroxyl-bearing carbon atom, —CH₂OH, is oxidized to form a



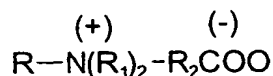
group); b is a number of from 0 to 3x+1 preferably an average of from 0.5 to 2 per glycosal group; p is 1 to 10, M¹ is H⁺ or an organic or inorganic counterion, particularly cations such as, for example, an alkali metal cation, ammonium cation, monoethanolamine cation, or calcium cation.

- 20 As defined in Formula I above, R is generally the residue of a fatty alcohol having from about 8 to 30 and preferably 8 to 18 carbon atoms. Examples of such alkylglycosides as described above include, for example, APG™ 325 CS Glycoside® which is described as being a 50% C₉-C₁₁ alkyl polyglycoside, also commonly referred to as D-glucopyranoside, (commercially available from Henkel Corp, Ambler PA) and
25 Glucopon™ 625 CS which is described as being a 50% C₁₀-C₁₆ alkyl polyglycoside, also commonly referred to as a D-glucopyranoside, (available from Henkel Corp., Ambler PA).

The nonionic surfactants, when present, can be present either singly, or as a mixture of two or more nonionic surfactant compounds as defined above.

- 30 As further useful optional constituent, the inventive compositions may also include one or more further known art surfactant compositions, including betaines, ethylene oxide condensates, fatty acid amides, and amine oxide semi-polar nonionic surfactants.

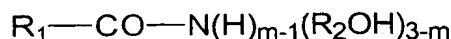
- 35 Exemplary useful betaine surfactants include those according to the general formula:



wherein R is a hydrophobic group selected from the group consisting of alkyl groups containing from about 10 to about 22 carbon atoms, preferably from about 12 to about 18 carbon atoms, alkyl aryl and aryl alkyl groups containing a similar number of carbon atoms with a benzene ring being treated as equivalent to about 2 carbon atoms, and similar structures interrupted by amido or ether linkages; each R₁ is an alkyl group containing from 1 to about 3 carbon atoms; and R₂ is an alkylene group containing from 1 to about 6 carbon atoms.

Examples of preferred betaines are dodecyl dimethyl betaine, cetyl dimethyl betaine, dodecyl amidopropyldimethyl betaine, tetradecyldimethyl betaine, tetradecylamidopropyldimethyl betaine, and dodecyldimethylammonium hexanoate.

Useful fatty acid amides include those which are known to the art. Particular exemplary fatty acid amide surfactants include ammonia, monoethanol, and diethanol amides of fatty acids having an acyl moiety which contains from about 8 to about 18 carbon atoms, and which may be represented in accordance with the formula:



where R₁ represents a saturated or unsaturated aliphatic hydrocarbon radical of from about 7 to 21 carbon atoms, but preferably from about 11 to 17 carbon atoms; R₂ represents a -CH₂- or -CH₂CH₂-, and m is an integer from 1 to 3, but is preferably 1. Preferably, R₁ is a saturated or unsaturated aliphatic hydrocarbon radical comprising from about 11 to 17 carbon atoms, and m is 1.

Further examples of such compounds include mono-ethanol amine coconut fatty acid amide and diethanol amine dodecyl fatty acid amide. An exemplary useful fatty acid amide includes cocomonoeethanol amide or cocodiethanolamide, which are presently commercially available as MONAMID CMA or MONAMID MDNA (both from Mona Industries, Paterson NJ (USA)).

It is also to be understood, that proportions of one or more constituents have been and generally are referred to as percent by weight or as parts by weight based on a measure of 100 % by weight, unless otherwise indicated.

According to certain particularly preferred embodiments of the first aspect of the invention there are provided aqueous concentrated liquid compositions which comprise (or preferably, consist essentially of) the following constituents:

According to certain particularly preferred embodiments of the first aspect of the invention there are provided aqueous concentrated liquid disinfectant compositions which comprise (or preferably, consist essentially of) the following constituents:

- 1 - 12 %wt. of pine oil constituent, preferably having at least 60% terpene alcohols;
- 0.5 - 8 %wt. of a germicidal cationic surfactant, preferably a quaternary ammonium compound having germicidal properties;

- 0.1 – 35 %wt. of an organic solvent constituent, preferably both an alkylene glycol and a monohydric lower aliphatic alcohol
0.2 – 4 %wt. of a binary co-solvent system comprising an alkyl diphenyl solvent and a co-solvent;
5 0 - 20 %wt. of at least one optional constituent as described above; and,
to 100 %wt. water.

Certain particularly preferred embodiments of the first aspect of the invention are disclosed on Table 1.1 of the Examples.

- 10 According to certain particularly preferred embodiments of the second aspect of the invention there are provided aqueous concentrated liquid hard surface cleaning composition which comprise (or preferably, consist essentially of) the following constituents:

- 1 - 12%wt. of pine oil constituent, preferably having at least 60% terpene alcohols;
15 0.1 - 35%wt. of an organic solvent constituent;
0.1 - 12%wt. of a binary co-solvent system comprising alkyl diphenyl solvent and a co-solvent;
1-20 %wt. of an amine oxide surfactant constituent;
0 - 20 %wt. of at least one optional constituent as described above; and,
20 to 100 %wt. water.

Certain particularly preferred embodiments of the second aspect of the invention are disclosed on Table 1.2 of the Examples

- 25 According to certain particularly preferred embodiments of the third aspect of the invention there are provided aqueous concentrated liquid disinfectant composition which comprise (or preferably, consist essentially of) the following constituents:

- 1-12%wt. terpene solvent containing constituent;
0.5-8%wt. germicidal cationic surfactant, preferably a quaternary ammonium compound having germicidal properties;
0.1-15%wt. organic solvent constituent;
30 1-12%wt. binary co-solvent system comprising alkyl diphenyl solvent and a co-solvent;
1-20%wt. one or more nonionic surfactants;
0 - 20 %wt. of at least one optional constituent as described above; and,
to 100%wt. of water.

- 35 Certain particularly preferred embodiments of the third aspect of the invention are disclosed on Table 1.3 of the Examples

- The concentrated compositions of the first, second or third aspect of the invention as taught herein may be used without dilution, i.e., in concentrate:water concentrations of 1:0, to extremely dilute dilutions such as 1:10,000. Desirably, the
40 concentrate is diluted in the range of 1:0.1 - 1:1000, preferably in the range of 1:1 - 1:500 but most preferably in the range of 1:10 - 1:100. The actual dilution selected is

in part determinable by the degree and amount of dirt and grime to be removed from a surface(s), the amount of mechanical force imparted to remove the same, as well as the observed efficacy of a particular dilution.

5 In accordance with preferred embodiments of the invention, when a quantity of the concentrate compositions taught herein are added to a larger volume of water, a blooming characteristic is manifested. Such "blooming" may be broadly characterized as the formation of milky, creamy or cloudy appearance which is manifested when a dilutable composition is added to a larger volume or quantity of water. Such "blooming" may be alternately characterized as the reduction of transmitted light through an
10 amount of water by at least 30%, desirably by at least 40%, yet more desirably by at least about 50%, and yet most desirably by at least 60% or more when a dilution of the concentrate composition:water with the weight or volume ratio range of from 1:64 - 102 is formed, wherein the dilution is at 20°C (68°F). That such blooming may be attained without the use of pine oil fractions as is common in certain commercially available
15 pine oil containing preparations is surprising.

As has been noted, concentrate compositions according to preferred embodiments of the invention exhibit a long lasting blooming effect when they are diluted into a larger volume of water, especially when used to form (weight ratio) dilutions with water of concentrate:water of 1:64 at room temperature. Desirably, such
20 dilutions do not exhibit an increase in light transmittance in accordance with the measurement methods discussed in the Examples below, of more than 50% (based on the initial 'as mixed' value) during its initial three-day interval.

The concentrate compositions taught herein, and dilutions formed therefrom are useful in the cleaning and/or sanitization of hard surfaces.

25 In preferred embodiments of the first aspect of the invention, aqueous dilutions of the concentrated aqueous liquid disinfectant compositions exhibit antimicrobial efficacy against at least one of the following bacteria: *Staphylococcus aureus*, *Escherichia coli*, *Pseudomonas aeruginosa*, where the ratio of concentrate composition:water is 1:64 to 1:102. According to more preferred embodiments the
30 compositions exhibit efficacy against at least two of the following bacteria: *Staphylococcus aureus*, *Escherichia coli*, *Pseudomonas aeruginosa*, where the ratio of concentrate composition:water of 1:64 to 1:102. Such aqueous dilutions may be classified as "broad spectrum disinfectant" compositions. According to a still more preferred embodiment, aqueous dilutions of the concentrated aqueous liquid
35 disinfectant compositions of the first aspect of the invention exhibit antimicrobial efficacy against all three of the following bacteria: *Staphylococcus aureus*, *Escherichia coli*, *Pseudomonas aeruginosa*, where the ratio of concentrate composition:water of 1:64 to 1:102. Such aqueous dilutions may be classified as "hospital strength disinfectant" compositions. In each of these respective preferred, more preferred and
40 still more preferred embodiments described immediately above, those which exhibit antimicrobial efficacy at greater aqueous dilutions of the concentrated aqueous liquid

disinfectant compositions in water, such as at concentrate:water dilution ratios ratios of 1:102, are preferred over concentrate:water dilution ratios of 1:85, and still more preferred over concentrate:water dilution ratios of 1:64.

5 Such dilution ratios of concentrate:water as described above may be volume/volume basis, or a weight/weight basis.

The following examples below illustrate exemplary and among them preferred formulations of the compositions according to the first and second aspects of the invention.

10 Examples

A number of formulations were produced by mixing the constituents outlined on Tables 1.1, Table 2.1 and 3.1 by adding the individual constituents into a beaker of deionized water at room temperature which was stirred with a conventional magnetic stirring rod. The order of addition is not critical, but good results are obtained where
15 the surfactants are added to the water prior to Stirring continued until the formulation was homogenous in appearance. It is to be noted that the constituents might be added in any order, but it is preferred that water be the initial constituent provided to a mixing vessel or apparatus as it is the major constituent and addition of the further constituents thereto is convenient.

20 It is to be noted the compositions demonstrating the formulations according to the first aspect of the invention are provided on Table 1.1, those according to the second aspect of the invention are listed on Table 1.2 and those according to the third aspect of the invention are listed on Table 1.3

TABLE 1.1

	Comp.1	Ex.1.1	Ex.1.2	Ex.1.3	Ex.1.4	Ex.1.5	Ex.1.6	Ex.1.7	Ex.1.8	Ex.1.9
Pine Oil 80	8.30	8.30	8.30	8.30	8.30	8.30	8.30	8.30	8.30	8.30
isopropyl alcohol	12.00	12.00	12.00	9.00	12.00	12.00	12.00	12.00	12.00	12.00
Na2EDTA	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
propylene glycol	23.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
lauryl alcohol	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
BTC-8358 (80%)	---	5.00	---	5.00	5.00	5.00	5.00	5.00	5.00	5.00
BTC-835 (50%)	8.00	---	8.00	---	---	---	---	---	---	---
biphenyl solvent A	---	1.00	1.00	1.00	---	---	0.20	0.40	0.60	0.80
biphenyl solvent B	---	---	---	---	1.00	---	---	---	---	---
biphenyl solvent C	---	---	---	---	---	1.00	---	---	---	---
Colorant	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Fragrance	0.10	---	0.10	0.10	---	---	---	---	---	---
di water	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.

Pine Oil 80 was a pine oil preparation containing at least 80%wt. terpene alcohols.

BTC-8358 (80%) was n-alkyl dimethyl benzyl ammonium chloride, 80%wt. actives

BTC-835 (50%) was n-alkyl dimethyl benzyl ammonium chloride, 50%wt. actives

biphenyl solvent A was NUSOLV ABP-103 (Arristec, Inc.) is a mixture of alkyl biphenyls

biphenyl solvent B was SURE SOL 300 (Koch Chemical Co.) is a mixture of alkyl biphenyls, specifically diisopropyl biphenyls (65%), triisopropyl

biphenyls (30%) and other alkyl biphenyls (5%)

biphenyl solvent C was SURE SOL 300 (Koch Chem.Co.) is a mixture of alkyl biphenyls

Na2EDTA was the disodium salt of ethylenediaminetetraacetic acid

di water was deionized water

TABLE 1.2

	Ex.2.1	Ex.2.2	Ex.2.3	Ex.2.4	Ex.2.5	Ex.2.6	Ex.2.7
Pine Oil 80	8.30	8.30	4.00	4.00	4.00	4.00	4.00
Isopropyl alcohol	12.00	12.00	12.00	12.00	12.00	12.00	12.00
Na2EDTA	0.50	0.50	0.50	---	0.50	0.50	0.50
Propylene glycol	20.00	20.00	20.00	20.00	20.00	20.00	20.00
lauryl alcohol	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Tomah AO-728 special (50%)	14.00	---	14.00	14.00	14.00	14.00	14.00
Ammonyx CDO (30%)	---	15.00	---	---	---	---	---
Biphenyl solvent A	1.00	1.00	4.00	4.00	4.00	---	---
Biphenyl solvent B	---	---	---	---	---	4.00	---
Biphenyl solvent C	---	---	---	---	---	---	4.00
Alkylpolyoxycarboxylate	---	---	---	0.50	---	---	---
Colorant	0.03	0.03	0.03	0.03	0.03	0.03	0.03
di water	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.

Pine Oil 80 was a pine oil preparation containing at least 80%wt. terpene alcohols.

TomahAO-728 (50%) was bis-(2-hydroxyethyl C₁₂-C₁₅ alkyloxypropyl) amine oxide (50%wt. actives)

Ammonyx CDO (30%) was cocoamidopropyl dimethylamine oxide (30%wt. actives)

Biphenyl solvent A was NUSOLV ABP-103 (Arristec, Inc.) is a mixture of alkyl biphenyls

Biphenyl solvent B was SURE SOL 300 (Koch Chemical Co.) is a mixture of alkyl biphenyls, specifically diisopropyl biphenyls (65%), triisopropyl biphenyls (30%) and other alkyl biphenyls (5%)

Biphenyl solvent C was SURE SOL 330 (Koch Chemical Co.) is a mixture of alkyl biphenyls

Alkylpolyoxycarboxylate was Emcol CNP 110 (Witco Chem. Co.) which also aids in solubilizing the alkyl biphenyls in water

Na2EDTA was the disodium salt of ethylenediaminetetraacetic acid

di water was deionized water

TABLE 1.3

	Comp3A	Ex.3.1	Ex.3.2	Ex.3.3	Ex.3.4	Ex.3.5	Ex.3.6
Pine Oil 60	9.00	3.00	6.00	8.00	5.00	4.00	7.00
Isopropyl alcohol	12.00	12.00	12.00	12.00	12.00	12.00	12.00
GENAPOL 26-L-80	6.00	6.00	6.00	6.00	6.00	6.00	6.00
VARONIC LI-63	1.70	1.70	1.70	1.70	1.70	1.70	1.70
AMMONYX CDO Special	0.75	0.75	0.75	0.75	0.75	0.75	0.75
MONAMID 15-70W	2.00	2.00	2.00	2.00	2.00	2.00	2.00
BTC-835 (50%)	1.60	1.60	1.60	1.60	1.60	1.60	1.60
BTC-818 (50%)	1.00	1.00	1.00	1.00	1.00	1.00	1.00
benzyl alcohol	0.75	0.75	0.75	0.75	0.75	0.75	0.75
biphenyl solvent	---	6.00	3.00	1.00	4.00	5.00	2.00
citric acid	0.05	0.05	0.05	0.05	0.05	0.05	0.05
di water	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.

Pine Oil 60 was a pine oil preparation containing at least 60%wt. terpene alcohols (alpha terpineols)

Isopropyl alcohol, was propan-2-ol

GENAPOL 26-L-80, Linear C12-C16 alcohol ethoxylate, average of 9 moles of ethylene oxide (ex. Clariant)

VARONIC LI-63, was a PEG 30 glyceryl cocoate nonionic surfactant

AMMONYX CDO Special was a cocoamidopropyl dimethylamine oxide

MONAMID 15-70W was a lineolamide diethanolamine

BTC-835 (50%) was an n-alkyl dimethyl benzyl ammonium chloride, 50% actives

BTC-818 (50%) was a dialkyl dimethyl ammonium chloride, 50% actives

benzyl alcohol was phenylmethanol

biphenyl solvent was NUSOLV ABP-103, diisopropylbiphenyl solvent

Na2EDTA was the disodium salt of ethylene diamine tetraacetic acid

citric acid, was anhydrous citric acid

di water was deionized water

TABLE 1.3

	Ex.3.7	Ex.3.8	Ex.3.9	Ex.3.10	Ex.3.11
d-Limonene	4.00	4.00	3.00	5.00	6.00
Isopropyl alcohol	12.00	12.00	12.00	12.00	12.00
GENAPOL 26-L-80	6.00	6.00	6.00	6.00	6.00
VARONIC LI-63	1.70	1.70	1.70	1.70	1.70
AMMONYX CDO Special	0.75	0.75	0.75	0.75	0.75
MONAMID 15-70W	2.00	2.00	2.00	2.00	2.00
BTC-835 (50%)	1.60	1.60	1.60	1.60	1.60
BTC-818 (50%)	1.00	1.00	1.00	1.00	1.00
benzyl alcohol	0.75	0.75	0.75	0.75	0.75
biphenyl solvent	3.50	3.00	4.00	2.00	1.00
Na2EDTA	1.50	1.50	1.50	1.50	1.50
citric acid	0.05	0.05	0.05	0.05	0.05
di water	q.s.	q.s.	q.s.	q.s.	q.s.

d-Limonene, was a monoterpene containing at least 90%wt. of d-limonene

Isopropyl alcohol, was propan-2-ol

GENAPOL 26-L-80, Linear C12-C16 alcohol ethoxylate, average of 9 moles of ethylene oxide (ex. Clariant)

VARONIC LI-63, was a PEG 30 glyceryl cocoate nonionic surfactant

AMMONYX CDO Special was a cocoamidopropylmethylamine oxide

MONAMID 15-70W was a lineolamide diethanolamine

BTC-835 (50%) was an n-alkyl dimethyl benzyl ammonium chloride, 50% actives

BTC-818 (50%) was a dialkyl dimethyl ammonium chloride, 50% actives

benzyl alcohol was phenylmethanol

biphenyl solvent was NUSOLV ABP-103, diisopropylbiphenyl solvent

Na2EDTA was the disodium salt of ethylene diamine tetraacetic acid

citric acid, was anhydrous citric acid

di water was deionized water

All of the formulations on Tables 1.1, 1.2 and 1.3 indicated weight percent, and the percent actives of individual constituents are 100% unless otherwise indicated.

The blooming characteristics of certain compositions described on Tables 1.1 and 1.2 was characterized by using the Brinkman Sybron PC 801 colorimeter. Each tested formulation were diluted with deionized water in a weight ratio of 1:64, and the test was carried out with each of the formulations and water at room temperature (68°F, 20°C). The resulting determined values, reported as "blooming" in the following table provide an empirical evaluation in percent transmittance (%) of the degree of transparency of a diluted example formulation wherein 0% indicates complete opacity and 100% the transparency of a deionized water sample. The result was tabulated as follows:

TABLE 2	
Formulation:	% Transmittance
Comp.1	26.2
Ex.1.1	1.1
Ex.1.2	0.9
Ex.1.3	3.6
Ex.1.4	1.8
Ex.1.5	1.9
Ex.1.6	3.0
Ex.1.7	2.7
Ex.1.8	2.2
Ex.1.9	1.3
Ex.2.1	2.4
Ex.2.2	3.1
Ex.2.3	0.7
Ex.2.4	0.9
Ex.2.5	0.5
Ex.2.6	0.7
Ex.2.7	0.9

Comparative 1 (Comp.1) was as indicated on Table 1.1, above.

As may be seen from the results indicated on Table 2, the formulation according to comparative example 1 (Comp.1) which did not include the biphenyl solvent did not give intense "bloom". In contrast, the formulations according to the first and second aspects of the invention provided an excellent blooming effect.

The formulations of Ex. 1.2, 2.3, 2.4 and 2.5 were diluted with deionised water in a weight ratio of 1:64, at room temperature (68°F, 20°C), and the degree of transparency was determined using the apparatus and method described above. For comparative purposes, a formulation ("Comp. 3") from the prior art, namely Ex. 3 from Table 1 of US 5629280 was prepared in accordance with the teaching in that patent, and similarly diluted and tested. These diluted formulations were evaluated over an eight day period at intervals so to determine the long term blooming behaviour of the

respective compositions. All of the formulations and compositions were maintained at room temperature (68°F, 20°C) throughout the duration of the test. The results are indicated on Table 3.

TABLE 3		
	% Transmittance	
Day:	Ex.1.2	Comp.3
Initial (as mixed)	1.2	5.9
Day 1	1.2	24.1
Day 2	1.2	29.6
Day 3	1.3	49.9
Day 6	1.4	76.1
Day 8	1.2	86.5

Comp. 3 was Ex. 3 from Table 1 of US 5629280

TABLE 3 (CONTINUED)			
	% Transmittance		
Day:	Ex.2.3	Ex.2.4	Ex.2.5
Initial (as mixed)	0.3	3.0	0.3
Day 1	0.3	3.7	0.4
Day 2	---	---	---
Day 3	---	---	---
Day 4	0.6	1.6	0.5
Day 5	0.5	1.5	0.7
Day 6	0.3	1.4	0.5
Day 7	0.4	1.3	0.5
Day 8	---	---	---

“---” indicates not tested, as it was visually observed that no discernible change had occurred since the previous test

As the results of Table 3 indicate, the compositions according to the present invention provided superior results, both with respect to initial blooming property in the “as mixed” dilutions, but also maintained excellent blooming characteristics over a longer duration.

The blooming characteristics of the formulations according to the third aspect of the invention were also characterized by using the Brinkman Sybron PC 801 colorimeter. Each tested formulation were diluted with deionized water in a weight ratio of 1:64, and the test was carried out with each of the formulations and water at room temperature (68°F, 20°C), as described above. Blooming characteristics of these formulations was evaluated both initially, and on a long term. All of the formulations and compositions were maintained at room temperature (68°F, 20°C) throughout the duration of the test. The results are indicated on Table 3.3.

Table 3.3

	Initial	1 hour	2 hours	4 hours	6 hours	24 hours	48 hours	72 hours	96 hours	168 hours
Comp.3A	70.7	75.1	75.7	76.3	76.9	81.4	83.3	86.7	89.4	93.7
Ex.3.1	98.7	93.5	87.0	76.0	68.5	26.0	10.8	5.3	3.2	1.3
Ex.3.2	99.8	99.8	99.7	99.4	99.9	100	99.1	99.4	99.2	99.8
Ex.3.3	67.3	76.3	77.4	78.4	79.0	82.7	82.4	84.7	85.7	88.6
Ex.3.4	99.9	98.8	96.7	93.4	91.8	75.4	66.6	59.6	56.6	52.4
Ex.3.5	99.3	96.2	92.3	85.4	81.6	47.8	29.3	19.8	14.9	8.4
Ex.3.6	83.4	90.5	91.3	92.0	92.3	95.6	94.5	95.6	96.0	96.6
Ex.3.7	98.1	89.9	78.0	73.5	---	31.5	21.1	19.4	---	23.2
Ex.3.8	98.6	91.3	85.0	76.0	---	39.5	40.6	53.0	---	78.8
Ex.3.9	98.3	90.4	83.7	73.9	---	27.4	14.7	11.3	---	8.9
Ex.3.10	98.1	90.1	82.2	71.9	---	50.3	79.7	92.5	---	100
Ex.3.11	99.5	100	99.6	100	---	100	100	100	---	100

--- indicates that the light transmittance was not tested for the indicated time interval

As may be seen from the results indicated on Table 3.3, the formulations according to the third aspect of the invention provided comparable or superior initial and short term (viz., to 2 hours) blooming when diluted in a larger quantity of water a compared to the formulation of Comp. 3A which included 9% of the pine oil constituent, but no biphenyl solvent. Further, certain of the dilutions of the concentrate compositions according to the invention which included the biphenyl solvent but which had reduced amounts of pine oil constituents provided excellent retention of blooming, particularly evidenced in the latter days of the test.

Antimicrobial efficacy

A modified European suspension test was carried out for formulations according to the first aspect of the invention, Examples 1.1, and 1.2 described above and as a comparative example, DETTOL (ex. Reckitt & Colman PLC, England). The method is summarized as follow.

- 1) Pipette 8 ml of the test product dilution into sterile medicant tube and held at 20C + 1C in water bath.
 - 2) In another sterile medicant tube pipette 1.0 ml of adjusted culture and 1.0 ml of prepared Bovine Albumin Solution and held at 20C + 1C in water bath.
 - 3) At time =0 minute, add product solution into medicant tube containing a mixture of Bovine Albumin Solution and culture suspension of each test organism. This mixture results in a final dilution of the test product, a concentration of 0.03% of Bovine Albumin Solution and bacterial count of at least $1-3 \times 10^7$ CFU/ml.
 - 4) At time =5 minutes, pipette 1 ml of this mixture into 9 ml of neutralizing solution (letheen broth) so as to achieve 1:10 dilution. Prepare serial dilution in Letheen broth and place with Trypticase soy with lecithin and Tween 80 agar in duplicate.
- Control: The procedure as outlined above was repeated, using 8 ml of sterile water instead of product dilution for each test organism.

To pass the test method, it was required that the tested formulations satisfy a 5 log reduction in reference bacterial strain of *S.aureus* (ATTC #5438), *Ps.aeruginosa* (ATTC #15442), *Escherichia coli* (ATTC #10536), with 5 minutes contact time at 20°C + 1°C under defined testing method. It was found that each of the formulations (Ex.1, Ex.2) showed complete reduction of the test organisms at the testing contact time. The testing requirements indicate a (great than) ">5" log reduction within 5 minutes. All the above samples exceed this requirement. It was concluded that formulations according to Ex. 1.1 and 1.2 have at least the same microbial activity as DETTOL.

Several of the exemplary formulations described in more detail on Table 1 above were evaluated in order to evaluate their antimicrobial efficacy against *Staphylococcus aureus* (gram positive type pathogenic bacteria) (ATCC 6538), *Salmonella choleraesuis* (gram negative type pathogenic bacteria) (ATCC 10708), and *Pseudomonas aeruginosa* (gram negative type pathogenic bacteria) (ATCC 15442).

The testing was performed in accordance with the protocols outlined in "Use-Dilution Method", Protocols 955.14, 955.15 and 964.02 described in Chapter 6 of "Official Methods of Analysis", 16th Edition, of the Association of Official Analytical Chemists; "Germicidal and Detergent Sanitizing Action of Disinfectants", 960.09 described in Chapter 6 of "Official Methods of Analysis", 15th Edition, of the Association of Official Analytical Chemists; or American Society for Testing and Materials (ASTM) E 1054-91 the contents of which are herein incorporated by reference. This test is also commonly referred to as the "AOAC Use-Dilution Test Method".

As is appreciated by the skilled practitioner in the art, the results of the AOAC Use-Dilution Test Method indicates the number of test substrates wherein the tested organism remains viable after contact for 10 minutes with at test disinfecting composition / total number of tested substrates (cylinders) evaluated in accordance with the AOAC Use-Dilution Test. Thus, a result of "0/60" indicates that of 60 test substrates bearing the test organism and contacted for 10 minutes in a test disinfecting composition, 0 or 1 test substrates had viable (live) test organisms at the conclusion of the test. Such a result is excellent, illustrating the excellent disinfecting efficacy of the tested composition.

Results of the antimicrobial testing are indicated on the Table, below. The reported results indicate the number of test cylinders with live test organisms/number of test cylinders tested for each example formulation and organism tested.

Table – Antimicrobial Efficacy		
Formulation	<i>Staphylococcus aureus</i>	<i>Salmonella choleraesuis</i>
Ex.1	0/60	0/60
Ex.2	0/60	0/60
Ex.3	1/60	0/60

As may be seen from the results indicated above, the compositions according to the invention provide excellent sanitizing benefits to hard surfaces as demonstrated by the excellent antimicrobial efficacy of these compositions against known bacteria

Cleaning Test:

Cleaning efficacy was measured for weight ratios of 1:64 (concentrate composition:water) aqueous dilutions of various formulations according to the invention, as well as a comparative composition. The test was carried out using the ASTM D4488-89, Annex A2 method - greasy soil on painted masonite wallboard test, using a Gardner Washability Apparatus.

Latex painted masonite wallboard is soiled with a mixture of melted, oily soils containing a small amount of carbon black and allowed to set overnight. A first aqueous dilution is applied to a sponge that scrubs half the soiled substrate in a straight-line using the Gardner Washability Apparatus. Afterwards, the second

aqueous dilution is applied to a further sponge that scrubs the other half of the soiled substrate in a similar manner.

In determining the cleaning efficiency, reflectance values were determined using a Gardner Lab Scan Reflectometer for each of the following: a clean unsoiled panel, a soiled panel, and a soiled panel following Gardner Washability Apparatus scrubbing. Such reflectance values were then employed to calculate % cleaning efficiency according to the following formula:

$$\% \text{ Cleaning Efficiency} = \frac{L_t - L_s}{L_o - L_s} \times 100\%$$

wherein,

L_t = % reflectance average after scrubbing solid tile

L_s = % reflectance average before cleaning soiled tile

L_o = % reflectance average original tile before soiling

Cleaning efficiency results for Formulation 1 are shown in TABLE 4, hereinafter.

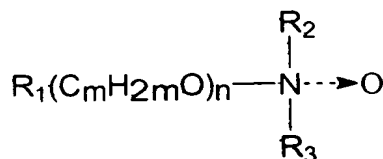
TABLE 4					
Test #	Formulation: water (1:64) w/w dilution	unsoiled reflectance (L_o)	soiled reflectance (L_s)	After scrubbing reflectance (L_t)	% Cleaning Efficiency
Comp.A	1:64	94.09	24.89	65.26	58.34
Ex.1.2	1:64	94.03	25.72	56.10	44.5
Ex.2.1	1:64	94.09	24.89	66.41	60.00
Ex.2.2	1:64	94.09	24.89	60.49	51.45
Ex.2.3	1:64	94.09	24.89	63.06	55.16
Ex.3.1	1:64	93.58	27.73	66.89	59.47
Ex.3.2	1:64	93.19	25.44	66.34	60.37
Ex.3.3	1:64	93.70	27.20	67.06	59.94

Comparative A (Comp.A) was DETTOL (Reckitt & Colman PLC, Hull, UK), a soap based, blooming type disinfecting concentrate composition which does not include biphenyl solvents. DETTOL has a particularly substantive bloom and is used as a 'benchmark' for other formulations.

As shown, the measurement of the cleaning effectiveness of the test samples involved the ability of the cleaning composition to remove the test soil from the test substrate. This was expressed by % Cleaning Efficiency. As numerical values for a % Cleaning Efficiency increase, higher cleaning effectiveness is achieved for the cleaning composition tested. As the results show, the inventive composition showed an excellent cleaning property.

Claims:

1. An aqueous concentrated liquid hard surface cleaning composition which
 5 blooms when added to a larger volume of water which comprises:
 a terpene based solvent or a pine oil constituent;
 optionally, a germicidal cationic surfactant;
 an organic solvent constituent;
 a binary co-solvent system comprising alkyl diphenyl solvent and a co-solvent;
 10 and,
 optionally an amine oxide surfactant;
 optionally a nonionic surfactant;
 optionally but desirably at least one optional constituent selected from:
 chelating agents, coloring agent, light stabilizers, fragrances, thickening agents,
 15 hydrotropes, pH adjusting agents, pH buffers one or more deterative surfactant
 constituents, and
 water.
2. The aqueous concentrated liquid disinfectant composition according to claim 1
 20 which includes a pine oil constituent which comprises at least 60% terpene
 alcohols.
3. The aqueous concentrated composition according to claim 1 which comprises
 amine oxide surfactant represented by the formula:



25

wherein

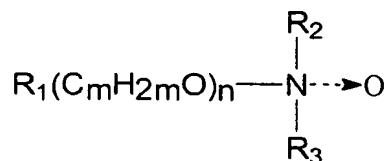
R₁ is hydrogen or is an alkyl, 2-hydroxyalkyl, 3-hydroxyalkyl, or 3-alkoxy-2-hydroxypropyl radical where the alkyl and alkoxy parts contain from about 8 to about 18 carbon atoms,

30

R₂ and R₃ are independently selected from methyl, ethyl, propyl, isopropyl, 2-hydroxyethyl, 2-hydroxypropyl, or 3-hydroxypropyl,
 m is an integer from 2 to 4, and

n is an integer from 0 to 10.

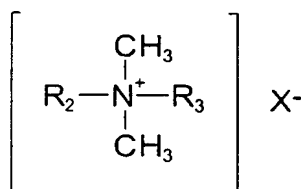
4. The aqueous concentrated composition according to claim 3 wherein the amine oxide constituent is represented by the formula:



wherein, R_1 is an alkyl radical of from 12 to 16 carbon atoms,
 R_2 and R_3 are independently selected from methyl or ethyl,
 m is 2, and
 n is 0.

5. A composition according to claim 1 which includes a quaternary ammonium compound as the germicidal cationic surfactant.

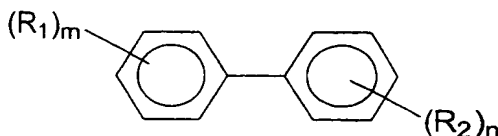
6. A composition according to claim 5 which includes as the germicidal cationic surfactant, a quaternary ammonium compound which may be represented by the formula:



wherein

R_2 and R_3 are the same or different C_8 - C_{12} alkyl groups, or R_2 is C_{12-16} alkyl, C_{8-18} alkylethoxy, C_{8-18} alkylphenoethoxy when R_3 is benzyl, and
 X is a halide.

7. The aqueous concentrated liquid disinfectant composition according to any preceding claim, wherein the alkyl diphenyl solvent is represented according to the structure:



wherein:

R_1 is hydrogen or is a lower alkyl radical, preferably a C_1 - C_{10} , but more preferably is a C_1 - C_6 straight chained or branched alkyl radical,

5 R_2 is a lower alkyl radical, preferably a C_1 - C_{10} , but more preferably is a C_1 - C_6 straight chained or branched alkyl radical,

m is an integer from 1 – 3 inclusive; and,

n is an integer from 1 – 3 inclusive.

10 8. The aqueous concentrated composition according to claim 7 wherein:

R_1 is hydrogen,

m is 1,

n is an integer from 1 – 3 inclusive, and,

R_2 is a C_1 - C_6 straight chained or branched alkyl radical.

15

9. An aqueous concentrated composition according to any preceding claim characterized in that when the said concentrated composition is diluted with water at a weight ratios of concentrate:water of 1:64 at room temperature, the resultant composition exhibits a reduction in light transmittance of at least 50%.

20

10. An aqueous concentrated liquid disinfectant compositions according to claim 1 which comprises:

25

1 - 12 %wt. of pine oil constituent, preferably having at least 60% terpene alcohols;

0.5 - 8 %wt. of a germicidal cationic surfactant, preferably a quaternary ammonium compound having germicidal properties;

0.1 – 35 %wt. of an organic solvent constituent, preferably both an alkylene glycol and a monohydric lower aliphatic alcohol

30

0.2 – 4 %wt. of a binary co-solvent system comprising an alkyl diphenyl solvent and a co-solvent;

0 - 20 %wt. of at least one optional constituent as described above; and, to 100 %wt. water.

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11. An aqueous concentrated liquid disinfectant composition according to claim 1 which comprises:
- 1 - 12%wt. of pine oil constituent, preferably having at least 60% terpene alcohols;
 - 5 0.1 - 35%wt. of an organic solvent constituent;
 - 0.1 - 12%wt. of a binary co-solvent system comprising alkyl diphenyl solvent and a co-solvent;
 - 1-20 %wt. of an amine oxide surfactant constituent;
 - 0 - 20 %wt. of at least one optional constituent as described above; and,
 - 10 to 100 %wt. water.
12. An aqueous concentrated liquid disinfectant composition according to claim 1 which comprises:
- 15 1-12%wt. terpene solvent containing constituent;
 - 0.5-8%wt. germicidal cationic surfactant, preferably a quaternary ammonium compound having germicidal properties;
 - 0.1-15%wt. organic solvent constituent;
 - 1-12%wt. binary co-solvent system comprising alkyl diphenyl solvent and a co-
 - 20 solvent;
 - 1-20%wt. one or more nonionic surfactants;
 - 0 - 20 %wt. of at least one optional constituent as described above; and,
 - to 100%wt. of water.
13. A process for cleaning a hard which comprises the process step of:
- contacting the hard surface with a disinfecting effective amount of the composition according to any preceding claim.
14. A composition according to claim 1 substantially as described with reference to the Examples.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 98/22783

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D3/48 C11D3/18 C11D3/43 A01N33/12 //A01N65/00,
A01N25/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	WO 97 06230 A (RECKITT & COLMAN INC) 20 February 1997 see page 12, line 9 - line 10 see page 14, line 26 - line 29; claims 1,8; example 4B; table 1C ---	1-6,9-14
A	WO 96 06153 A (CIBA GEIGY AG) 29 February 1996 see claims 1,22 ---	1,7,8
A	DE 195 37 782 A (FOERSTER KARL HEINZ) 17 April 1997 see claims 1,3 -----	1,7,8



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search

26 February 1999

Date of mailing of the international search report

10/03/1999

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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